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**CAPILLARY RHEOMETRY FOR  
THERMOSETS**

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## THE FLOW BEHAVIOR OF THERMOSETS

The chemorheology of any thermosetting molding compound can be separated into two regions of interest by the concept of a gel point. Prior to gelation the resin is a flowable melt which can generally be described as a pseudoplastic material characterized by an apparent shear viscosity. The onset of gelation is signaled by a rapid increase in apparent viscosity. Beyond this point the material is best characterized by dynamic type mechanical measurements and calorimetry [1].

Thus before gelation the apparent viscosity of a thermosetting material is a function of time, temperature and shear rate [1-7]. Behavior subsequent to gelation, since no flow is involved, depends only on time and temperature. Thermosets exhibit a characteristic "U" shaped curve when the apparent viscosity is plotted versus time or temperature for a fixed shear rate. The downward part of the curve is representative of thermal softening and pseudoplastic flow. A minimum is reached and then a rapid increase in viscosity caused by the crosslinking reaction is observed. A great deal of information concerning processing behavior can be determined from such viscosity-time-temperature profiles: maximum residence time in the screw barrel, mold curing time, minimum viscosity and the temperature sensitivity of the material [1]. A plot of apparent viscosity as a function of shear rate for different temperatures also provides important information for understanding mold filling.

The shear viscosity will also be affected by a number of other considerations. Moisture can greatly reduce the apparent viscosity and lead to blistering and porosity in the molded part [8]. Fillers can change the shear viscosity in two ways. The pseudoplastic behavior prior to gelation can be affected by filler geometry, type, surface treatment and concentration. The kinetics of crosslinking can be influenced by reactive complexes on the filler's surface [9]. Additives can also change the viscosity [10] and thermal stability [11].

## TECHNIQUES FOR MEASURING SHEAR VISCOSITY IN THERMOSETS

A number of techniques have been used to characterize the flow behavior of thermosets. Among the most popular have been spiral flow molds [8,12,13], minimum pressure to fill a cavity [14], Brabender and other type torque rheometers [6,14-16], cone and plate rheometers [1,3,17], injection molding machine operations [15,17,18], and capillary rheometers [2,19].

Many of the above techniques require the use of injection molding machines and give at best semi-quantitative

results. Other methods are restricted to low shear rate measurements which may not give a good indication of the material's behavior in actual processing. A simple and effective means of evaluating thermoset flow behavior which would provide quantitative results directly applicable to process engineering would be most welcome.

The capillary rheometry technique is well established, convenient, and the only method able to yield shear viscosity data at the high shear rates characteristic of the injection molding process. However, the use of this technique with thermosets can encounter a number of problems. Temperature control is much more critical with thermosets than with thermoplastics. Hot spots in the barrel or capillary can lead to unwanted local curing. Cleaning the barrel of material which has set up can be a major problem.

Commercially available capillary rheometers have been designed exclusively for use with thermoplastic materials. Electric band heaters are used to maintain the barrel temperature and a rather limited maximum load is available to force material from the barrel. Therefore these devices are unsuitable for use with thermosets.

With these problems in mind a capillary rheometer was designed specifically for use with thermosets. A schematic representation of the system built is shown in Figure 1. The rheometer barrel was heated by circulating Dowtherm G® fluid from a process heat transfer system through a surrounding jacket. Temperatures up to 550°F (288°C) could be attained with the heating element used. Higher temperatures up to the fluid's maximum of 650°F (343°C) could be reached with a more powerful heating unit. Temperature control was provided by a proportional temperature regulator monitoring the temperature of the fluid in the barrel jacket. The variation in temperature from the set point was approximately 1°F at 500°F (260°C). Fluid entered the jacket at the bottom and exited near the top, thus insuring that the barrel would always be covered to the same level. The capillary itself was placed relatively high up in the barrel in order to insure that its temperature would be close to that of the surrounding fluid. Several samples which cured in the barrel showed smooth surfaces indicating that the temperature was uniform along the barrel.

The barrel-jacket assembly was attached to a movable frame which was inserted into a constant crosshead speed testing machine. Flexible stainless steel hoses allowed the barrel-jacket assembly to be separated from the heat transfer system. The testing machine used could provide up to 20,000 lbs of force. This allowed any material which set up in the barrel to be pushed out by the piston, since its length of travel could extend past the capillary position in

the barrel. Any material in the capillary was removed by the use of a thin steel rod.

## EXPERIMENTAL PROCEDURES

Standard techniques for capillary rheometry were used [20,21]. After the desired temperature was reached, the 3/8 inch diameter barrel was filled to a two inch level with the resin to be studied. The charge was then compacted under low force. It remained for a set period of time and then was pushed through the capillary with the ram descending at constant speed. The resulting force on the load cell was automatically plotted as a function of time.

The apparent viscosity  $\eta$  is given as

$$\eta = \frac{\tau_R}{\dot{\gamma}_R}$$

where  $\tau_R$  is the shear stress and  $\dot{\gamma}_R$  is the shear rate at the capillary wall. Ignoring entrance and exit effects

$$\tau_R = \frac{\Delta P R}{2L}$$

where  $\Delta P$  is the pressure drop across the capillary,  $R$  is the capillary's radius and  $L$  its length. The shear rate at the wall is given as

$$\dot{\gamma}_R = \frac{1}{\tau_R^2} \frac{1}{d\tau_R} (\tau_R^3 Q/\pi R^3)$$

where  $Q$  is the volumetric flow rate.

Thus the apparent viscosity can be calculated for various conditions of shear rate, temperature and time.

## EXPERIMENTAL RESULTS

Initial testing of the rheometer was conducted using thermoplastic materials. The equipment and the experimental techniques were verified. An alkyd type polyester injection molding compound by Hooker, 24668, was the first thermosetting material tested. A capillary of diameter 1/16" and length 1.25",  $L/D = 20$ , was used in all the tests discussed below.

The apparent viscosity as a function of shear rate at 230°F (110°C) and different heating times is shown in Figure 2. A power law type behavior is displayed at all values of heating time. There is no measurable effect of time on viscosity because at the test temperature the rate of crosslinking is very low. The same type of general behavior is displayed at 250°F (121°C) as shown in Figure 3. However, the viscosity is somewhat lower across the range of shear rates than at 230°F (110°C) showing a temperature dependence similar to

thermoplastics. The results obtained at 270°F (132°C) are shown in Figure 4. Again a power law type behavior is apparent. At this higher temperature the magnitude of the viscosity is lower at any fixed shear rate and heating time than in the two previous cases. The effect of heating time is more pronounced since the rate of crosslinking is greater at 270°F (132°C). In fact at a heating time of three minutes the sample cured sufficiently so that it could not be extruded.

The effect of temperature on viscosity with the shear rate and heating time constant is shown in Figure 5. At the heating time used only the decreasing portion of the "U" shaped curve is developed. A minimum in the viscosity curve is observed in Figure 6 which was obtained at 250°F (121°C). The shear rate seems to affect the magnitude of the viscosity but not the nature of its behavior with time.

By plotting viscosity against the inverse of absolute temperature at a fixed heating time and shear rate an apparent activation energy for viscous flow can be determined. The data of Figure 7 was obtained with a heating time of two minutes. Under these conditions the data seemed to indicate a shear rate dependence of the apparent activation energy. An average value of 7.8 Kcal/mole was calculated at low shear rates and 5.1 Kcal/mole at high shear rates.

## CONCLUSIONS

Capillary rheometry can be effectively used with thermosets if the equipment employed is designed to overcome some of the inherent problems of these materials. Most important is providing a uniform temperature in the barrel. This has been successfully accomplished by using a circulating hot oil system. Standard capillary rheometry methods can provide the dependence of thermoset apparent viscosity on shear rate, temperature and time. Such information is very useful in evaluating resin processability and in setting preliminary fabrication conditions.

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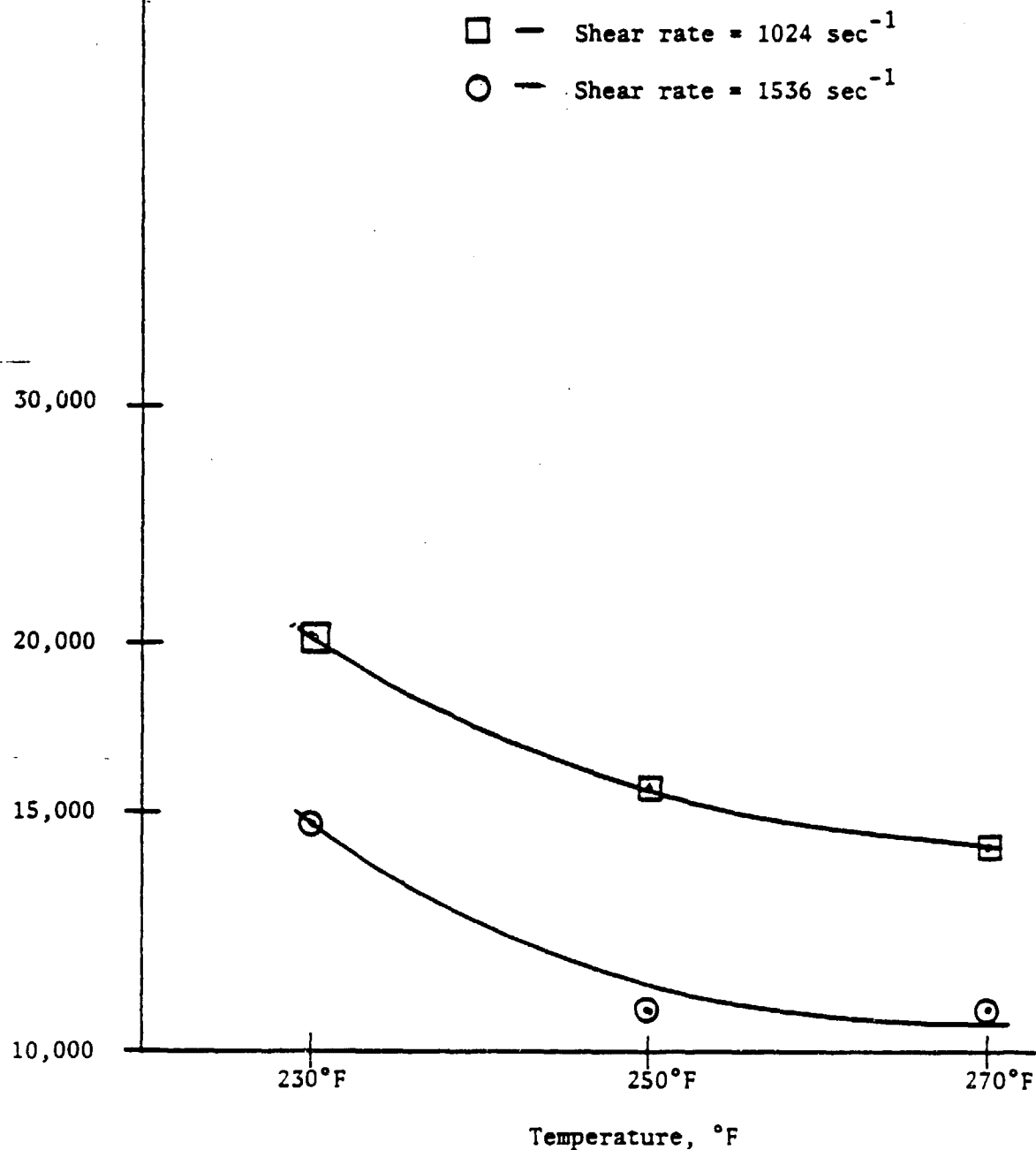


Figure 5. Viscosity as a function of temperature with a 2 minute heating time for an alkyd polyester.

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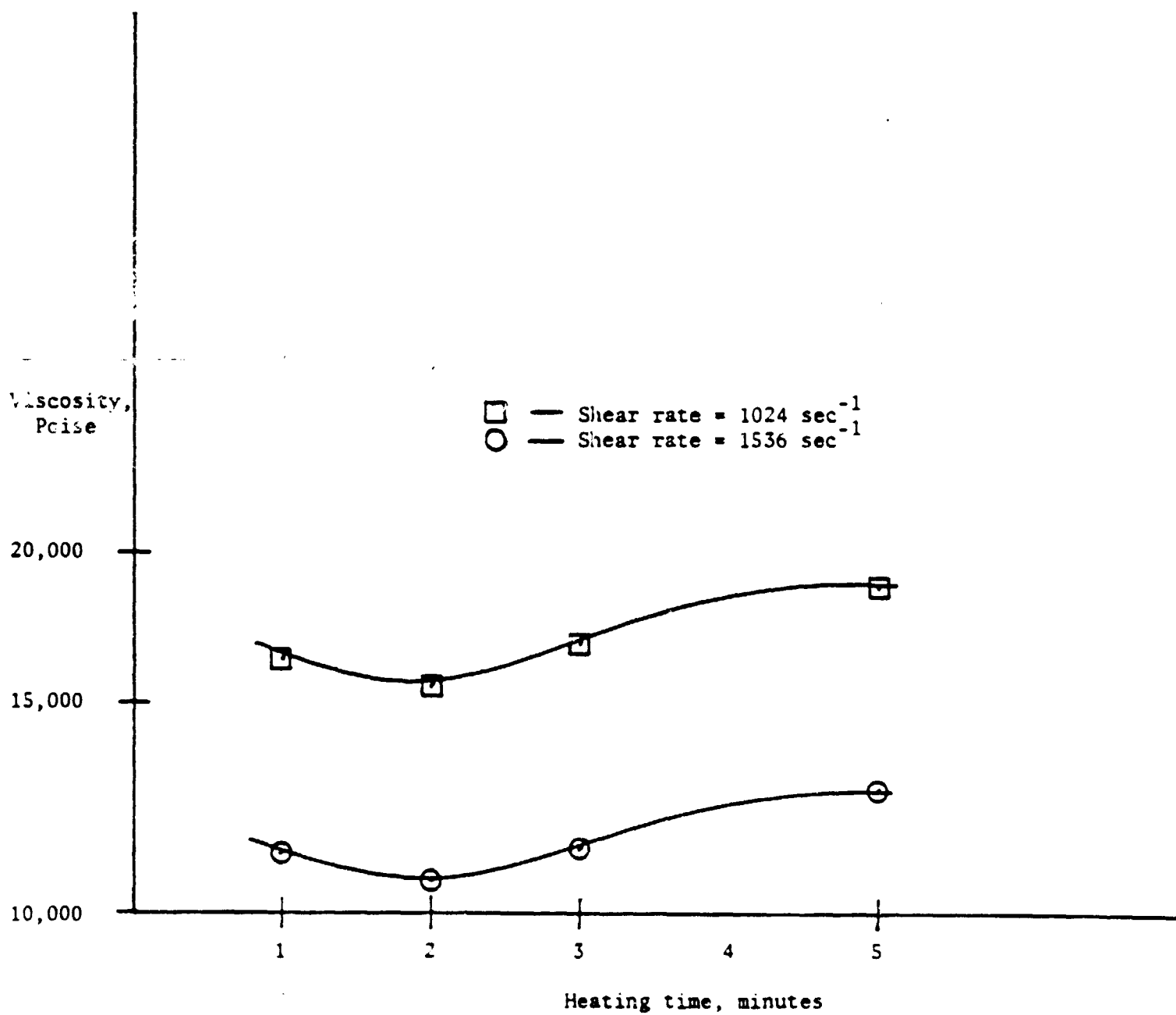


Figure 6. Viscosity as a function of heating time at 250°F for an alkyd polyester.

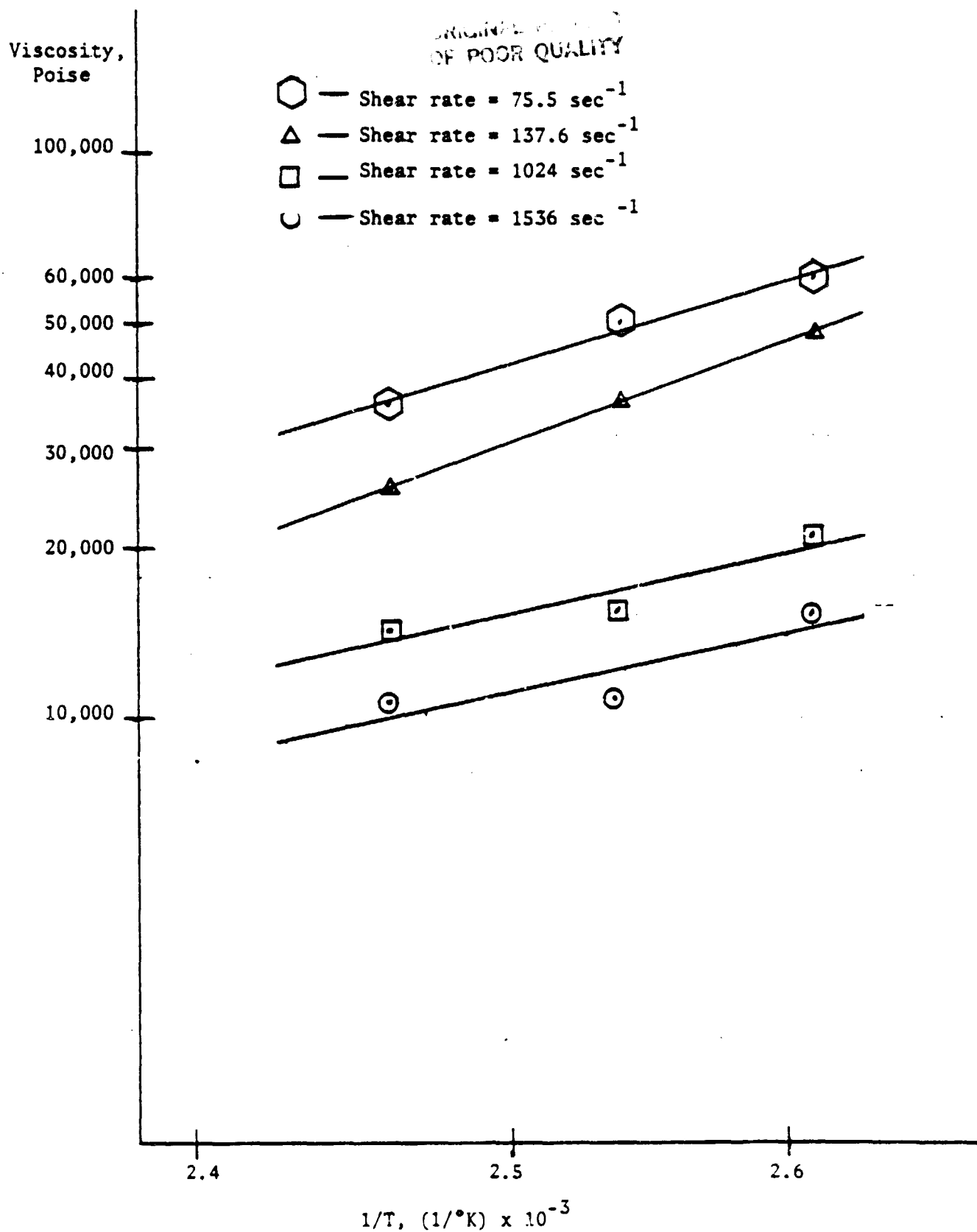


Figure 7. Viscosity as a function of inverse temperature with a heating time of 2 minutes for an alkyd polyester.

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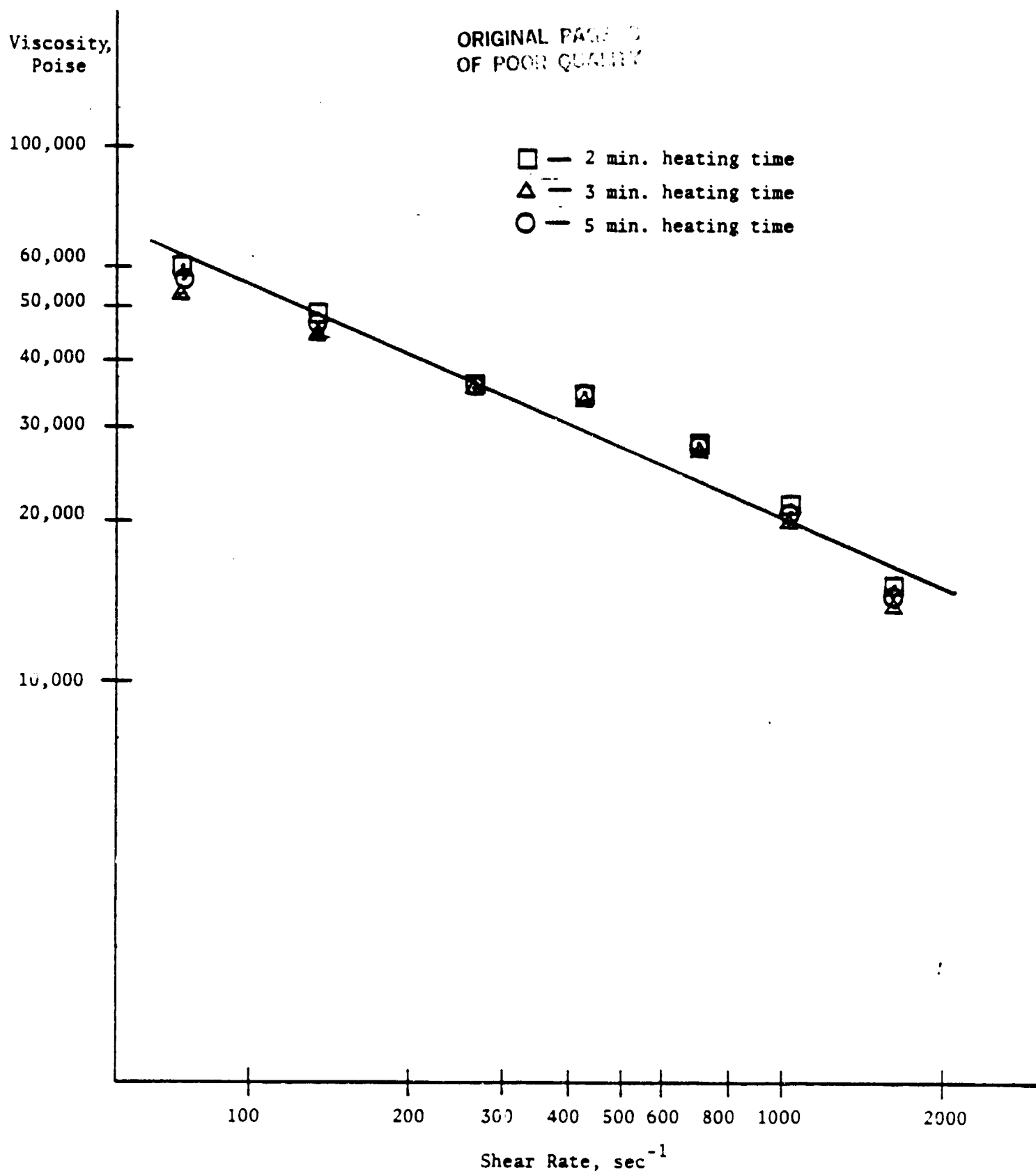


Figure 2. Effect of shear rate on viscosity at 230°F for an alkyd polyester.

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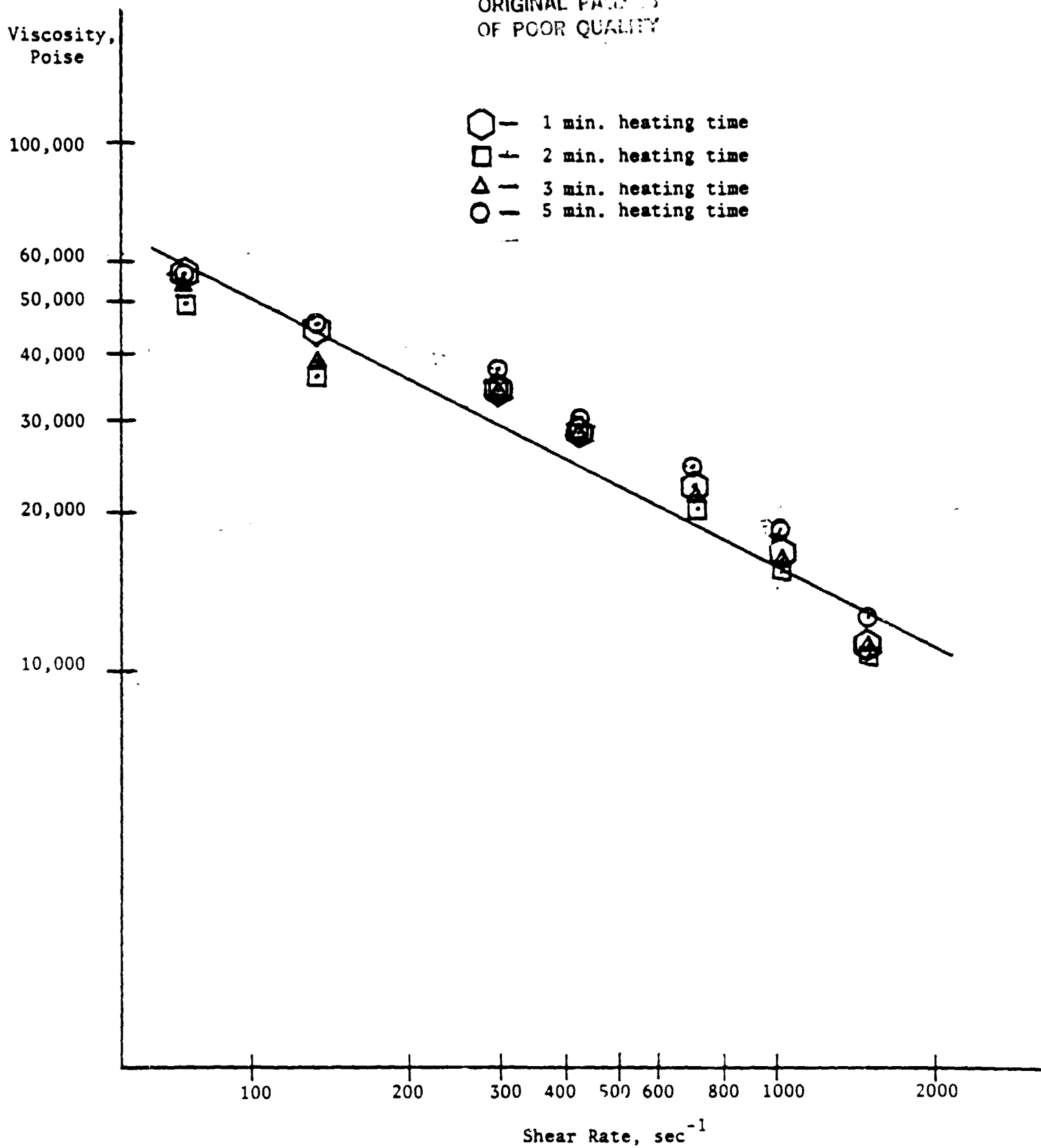


Figure 3. Effect of shear rate on viscosity at 250°F for an alkyd polyester.

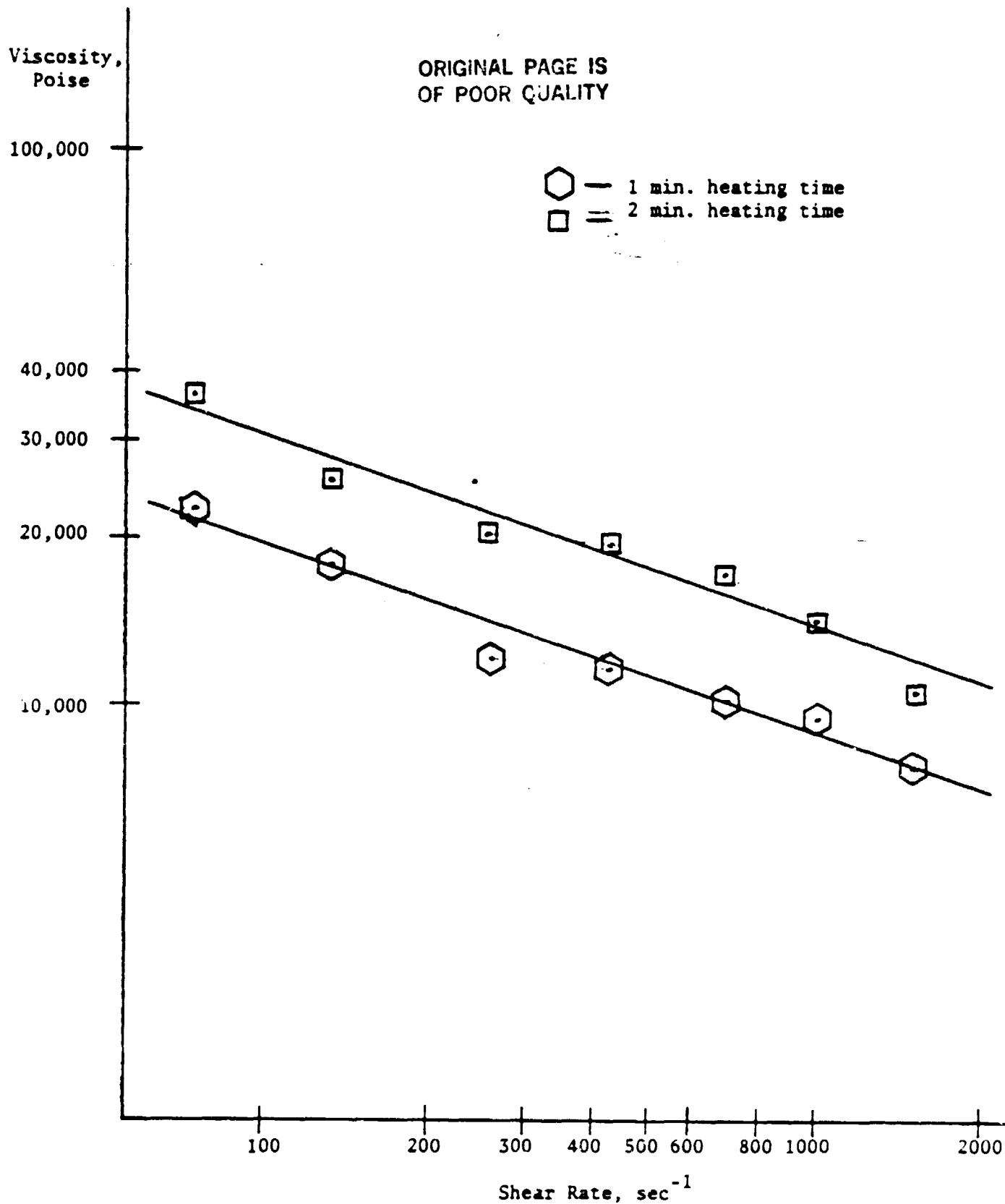


Figure 4. Effect of shear rate on viscosity at 270°F for an alkyd polyester.

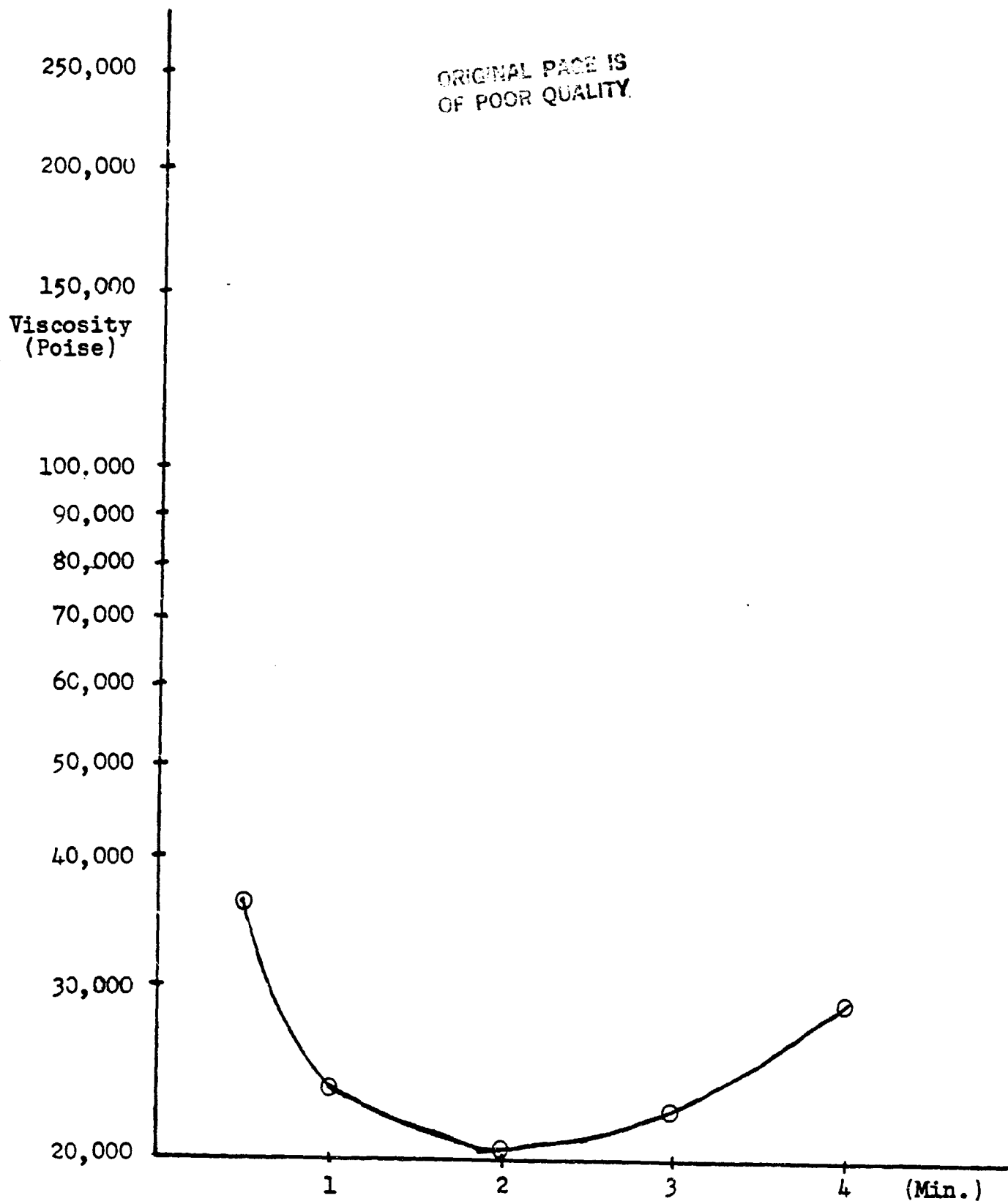


Figure 5. Effect of heating time on viscosity at 240°F and a shear rate of 153.6 sec.<sup>-1</sup> for a woodflour filled phenolic.

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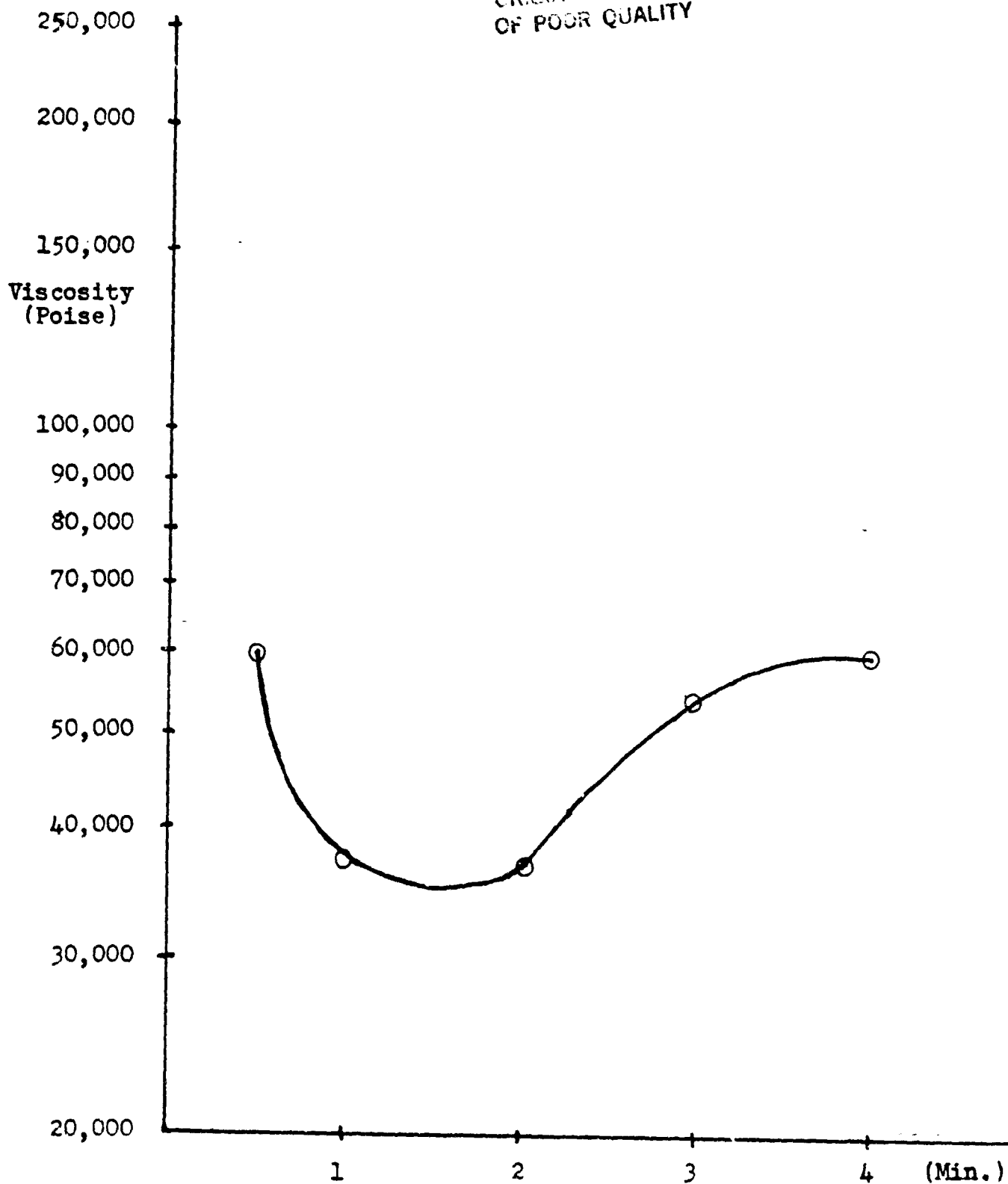


Figure 6. Effect of heating time on viscosity at 230°F and a shear rate of 81.2 sec.<sup>-1</sup> for a phenolic.



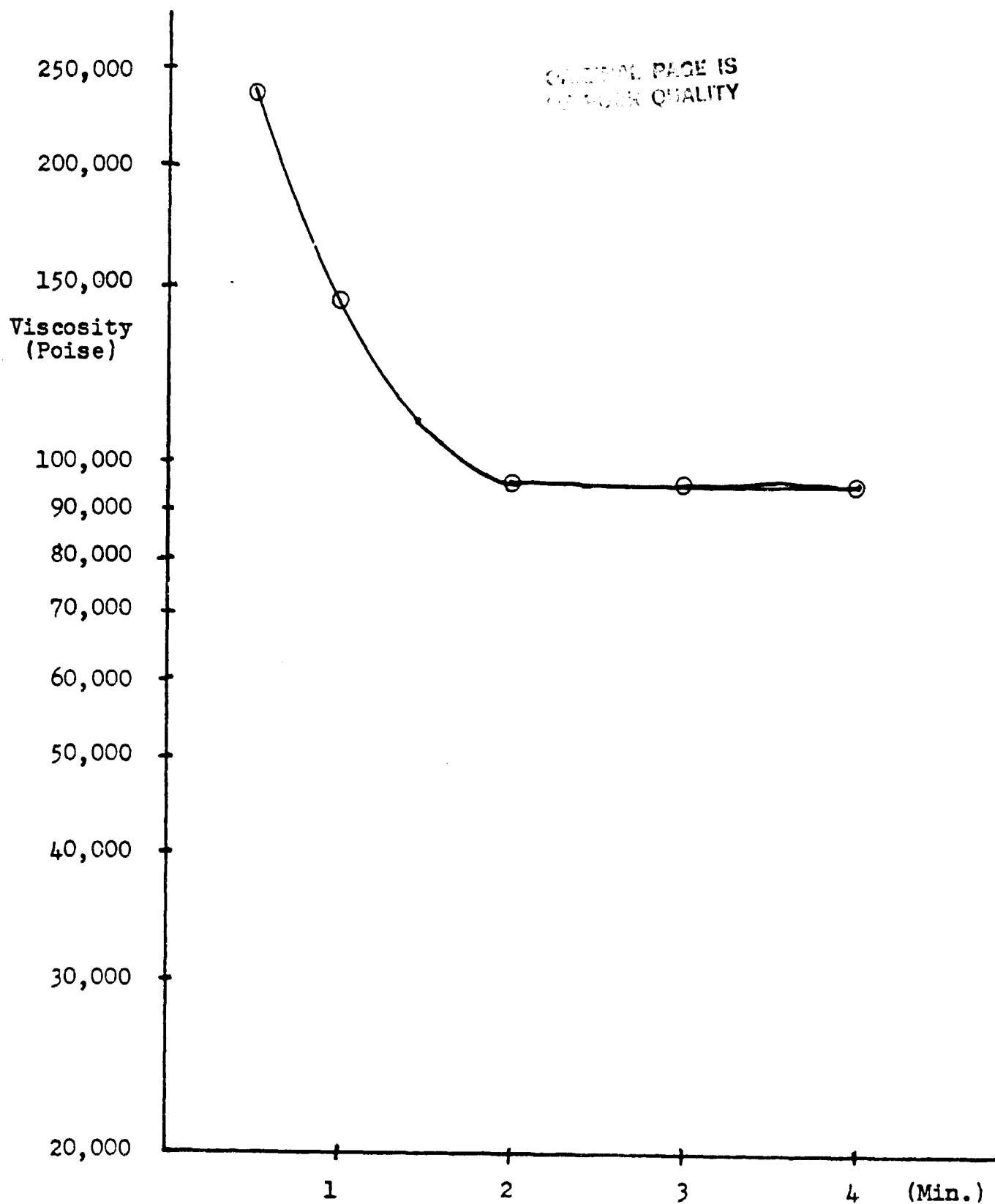


Figure 7. Effect of heating time on viscosity at 250°F and a shear rate of 81.2 sec.<sup>-1</sup> for a dially phthalate.